FLOW ENHANCEMENT IN PIPELINE TRANSPORTATION FOR HEAVY CRUDE OIL EMULSION

NURUL HAFIZA NORDEN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2014

ABSTRACT

Stable concentrated oil in water (O/W) emulsions was prepared and their application for heavy oil pipeline transportation was investigated using very viscous Malaysian heavy crude oil. Malaysian heavy crude oil samples namely Miri were used to produce heavy crude oil- in-water emulsions. Historically, demand for heavy and additional-heavy oil has been marginal because of their high viscosity and composition complexity that make them hard and expensive to produce, transport and refine. Presently, there are three general approaches for transportation of heavy and extra heavy oil which are viscosity reduction, drag minimization and in-situ oil enhancement .This 3 conventional method required high cost. Hence, our scope of study approached is to convert the 95% of w/o in pipeline to o/w technique by using the advantage of water to carry the oil .This method is a promising cost effective and shorten the time of the transportation .The expected result based on the reference was revealed that the stability of the oil-in-water emulsion stabilized by Triton X-100 increased as the surfactant concentration increases, with a consecutive decrease in the crude oil–water interfacial tension (IFT). Larger the oil content, the speed and duration of mixing, while increases in the temperature of the homogenization process substantially reduced the viscosity of the prepared emulsions.

Key words: SARA, crude oil, emulsion, separation, stability, transportation.

ABSTRAK

Kepekatan emulsi air di dalam minyak (O/W) yang stabil telah disediakan dan aplikasi untuk pengangkutan minyak berat dalam saluran paip minyak telah dikaji dengan menggunakan minyak mentah berat Malaysia yang sangat likat. Sampel minyak berat mentah Malaysia daripada Miri digunakan untuk menghasilkan minyak mentah dalam air emulsi. Dari segi sejarah, permintaan bagi minyak berat dan sangat berat telah marginal kerana kelikatan dan komposisi yang tinggi. Hal initelah merumitkan mereka dan mahal dalam penghasilan, pengangkutan dan menghalusi. Pada masa ini, terdapat tiga pendekatan untuk pengangkutan minyak berat iaitu dengan pengurangan kelikatan, meminimumkan seretan dan peningkatan minyak in-situ. 3 kaedah konvensional ini memerperlukan kos yang tinggi. Oleh itu, skop kajian didekati adalah untuk menukar 95% daripada w/o dalam jenis o/w dengan menggunakan teknik kelebihan air untuk menjalankan minyak. Kaedah ini akan menjanjikan kos yang efektif dan memendekkan masa pengangkutan. Hasil ini dijangkakan berdasarkan rujukan yang mendedahkan bahawa kestabilan emulsi minyak dalam air distabilkan oleh span 83 sebagai surfactant untuk meningkatan kepekatan dengan penurunan yang berturut-turut dalam ketegangan antara muka mentah minyak air (IFT). Yang lebih besar kandungan minyak, kelajuan dan tempoh pencampuran, sementara kenaikan suhu proses penyeragaman yang dikurangkan kelikatan emulsi bersedia.

Kata kunci: SARA , minyak mentah, emulsi, perpisahan, kestabilan, pengangkutan.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

ϒ	Shear Rate
τ	Shear Stress
v	Velocity of the fluid
μ	Viscosity

LIST OF ABBREVIATION

API	American Petroleum Institute
RPM	Revolution Per Minute
Span 80	Sorbitan Oleate
Span 83	Sorbitan Sesquioleate
Triton X-100	Octylphenolpoly (ethyleneglycolether)x
O/W	Oil-in-Water emulsion
O/W/O	Oil-in-Water-in-Oil emulsion
W/O	Water-in-Oil emulsion
W/O/W	Water-in-Oil-in-Water emulsion
HLB	Hydrophilic-Lipophilic Balance

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Motivation and statement of problem

The mixed of the downfall of conventional oils and an increase demand in world energy, crude oils was one of the list hydrocarbons resources that relevant for use in the future. Hydrocarbon resources are big considerable given that they account for approximately 65% of the world's overall energy resources. Currently, crude oil is the most important hydrocarbon resource in the world, and heavy crudes account for a large fraction of the world's potentially recoverable oil reserves (Abdurahman et al., 2012). Based on data collected by Herron., 2004, as depicted in Figure 1.1, worldwide deposits of heavy hydrocarbons are estimated to total almost 5½ trillion barrels, and four-fifths of these accumulated are in the Western Hemisphere. In the United States, heavy hydrocarbon deposits are estimated to be more than eight times that of the nation's remaining reserves of conventional crude oil.

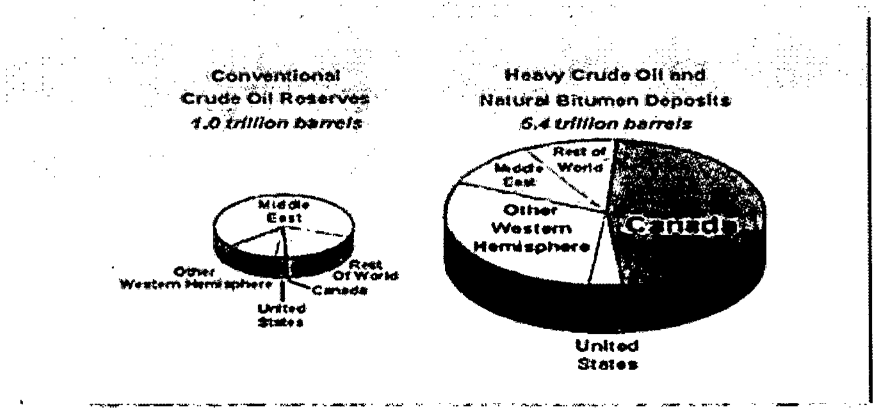

Figure 1.1 :Worldwide Distribution of Conventional Crude Oil and Heavy Hydrocarbons.

According to Ashrafizadeh et al., 2012, another favorable pipeline technique is the transport of viscous crudes oil as concentrated oil-in-water (O/W) emulsions. An emulsion is formed when two immiscible liquid are mixed together. The two basic type of emulsion consist of water-in-oil (w/o) and oil-in-water (o/w) (Fig.1.2). Somehow, in some cases multiple emulsions such as water-in-oil-water (w/o/w) and oil-in-water-in-oil (o/w/o) emulsions can be found. There are three main criteria that play important role during emulsification process (Masato Kukizaki et al., 2003).

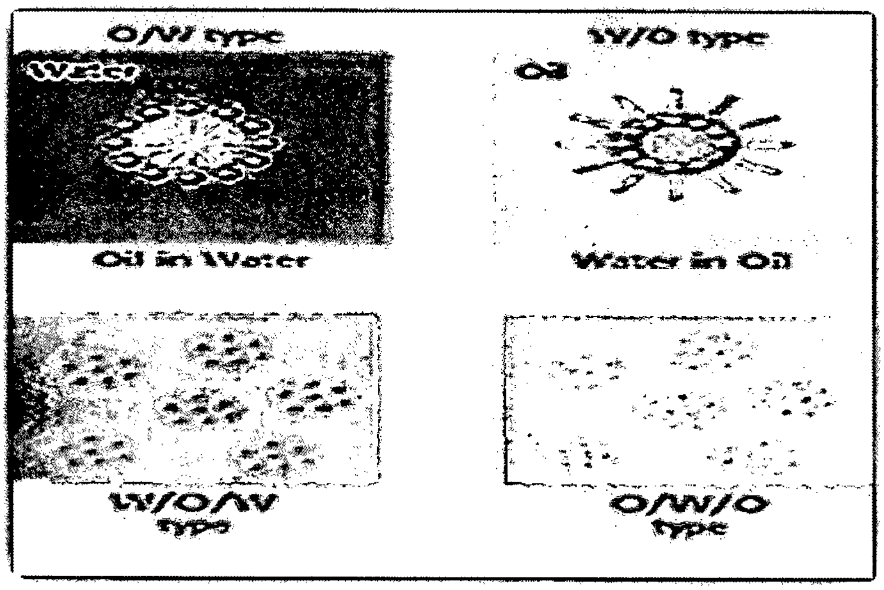

Figure 1.2: Type of Emulsion.

Heavy and extra heavy crude oils methods of transportation have a main challenge with their high viscosity. From 1975 to 2000, global demand for crude oil had growth rate about 1% average (Hoshyagar et al., 1012). 90% to 95% of the world crude oil is produced in the form of emulsion. The presence of water in oil creates a lot of problems, for economic and operational reasons, it is necessary to eliminate water completely from the crude oil emulsion before refining and transporting the crude oil because it will affect the pipeline (Nuraini et al., 2011).

Refer to N.H.Abdurahman at el., (2013), the formation of an emulsion significantly reduces the emulsion viscosity. Even an O/W emulsion might reduce corrosion for a crude oil with high sulfur content. N.H.Abdurahman at el. (2013) also stated that the produced emulsions have viscosities in the range of approximately 0.05-0.2 Pa.s. This reduction in viscosity decreases transportation costs and transport-related problems. Nowadays, Alberta in Canada and the Orinoco Belt in Venezuela are good examples of regions producing extra heavy oil. However, an increase in production of heavy and extra heavy crude oil will take place in several regions like the Gulf of Mexico and North eastern China, as it will be needed over the next two decades to replace the declining production of conventional middle and light oil. Therefore, there is a growing interest in the use of non-conventional heavy and extra heavy oil resources to produce fuels and petrochemicals. The incorporation of heavy oil to energy markets presents important challenges that require significant technological developments in the production chain. The transportation of heavy and extra-heavy oil presents many operational difficulties that limit their economic viability. Countries like China, Japan or the USA, with growing energy demands, promote the restructuration of its refining industries to handle this non-conventional crude. Nowadays, heavy and extra heavy oil are cheaper than conventional petroleum and the refining margin can be bigger if properly handled with higher profits per barrel. Pipelining is the most convenient mean for transportation of crude oils and derived products continuously and economically. However, transportation of heavy and extra heavy crude oils through pipelines is difficult due to the low mobility and flow ability of the crude and wax and asphaltene deposition on pipeline wall surfaces. Still, one of the technological issues regarding the access of extra heavy oil to energy markets is the problem of pipeline transportation as mentioned earlier (Rafael, María & Beatriz et al., 2011).

1.2 Objectives

The following are the objectives of this research:

- To investigate the factors affecting both the stabilization and the destabilization of Miri crude oil crudes oil in water emulsion in order to improve the flow enhancement.

- To investigate the performance of 2 type of amine functional group (Hexylamine and Octylamine) in destabilization of crude oil emulsion.

1.3 Scope of this research

The followings are the scope of this research:

1) Collecting the stable crude O/W samples for Malaysian oil samples which are from Miri refinery.
2) Experimental analysis of the influence of the type of oil, the viscosity, the size of the droplet water ,the optimum temperature, the sheer rate, the sheer stress, the speed(rpm), the torque, the surface tension and the interfacial tension.
3) To investigate the factors effect on reducing of viscosities of oil in water emulsion in pipeline transportation.
4) To study the influence of concentration of emulsifier and composition of o/w on the stabilization of heavy o/w emulsions.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

A good knowledge of petroleum emulsions is necessary for controlling and improve processes at all stages (Langevin et al., 2004). With increasing viscosity, the head loss due to friction increases. Therefore, greater pump horsepower is required. Thus, it is necessary to reduce the viscosity of the oil being transported. Crude oil can be fractionated into four different compounds, namely, saturated, aromatic, resins and asphaltenes (SARA). A reliable compositional characterization of petroleum fractions is important for the optimization of refining processes products performance evaluation structure property correlations, oil-supply correlations and environmental issues (Pasadakis et al., 1999).

According to Jeribi et al., 2002, emulsions with particles and asphaltenes connected can be much more stable than those stabilized by asphaltenes alone, supply that enough asphaltenes are present: all the adsorption sites on the particle surface need to be saturated by asphaltenes. The resin and asphaltene content using heptane SARA (Saturated, Aromatic, Resin, Asphaltene) analysis of various heavy crude oils are given in Table 2.1.

Table 2.1: SARA Analysis of the Crude and Elementary Composition of different Fractions: Saturates, Aromatics, Rasins and Asphaltenes

% weight	SARA pentene	SARA Haptene	%weight Haptene SARA fractions				
			C	H	N	O	S
Asphaltenes	17	14.1	83.8	7.5	1.3	1.7	4.8
Resins	33	37.3	82.8	8.9	1.5	2.0	4.3
Aromatics	37	37.2	84.3	10	<0.3	1.1	4.0
Saturated	12	11.4	86.6	13	<0.3	<0.2	<0.1

2.2 Formation of heavy and extra-heavy crude oil emulsions in water

According to Pilehvari 1988, emulsions naturally occur in petroleum production and pipelining, mainly those of water-in-oil (W/O) and more complex like oil-in water- in-oil (O/W/O) emulsions .Such emulsions are detrimental for oil production since oil's viscosity raises, increment corrosion issues and are difficult to break in desalting and dehydrating units before refining. Nevertheless, emulsions or dispersions of heavy or extra-heavy crude oil in water (O/W) or in brine may be an alternative to pipeline transportation of high-viscosity crudes because of viscosity reduction.

2.3 Crude Oil and Heavy Crude Oil

According to Calgary Chapter and Petronas society 2002, a mixture consisting mainly of pentanes and heavier hydrocarbons that exists in the liquid phases in reservoirs and remains liquid at atmospheric pressure and temperature. Crude oil may consist with sulphur and other non-hydrocarbon compounds, but does not include liquids obtained from the processing of natural gas. Classes of crude oil are frequently reported on the basis of density, sometimes with different meaning. Acceptable ranges are as follows:

- Light: less than 870 kg/m^3 (more than 31.1° API)
- Medium: 870 to 920 kg/m^3 (31.1° API to 22.3° API)
- Heavy: 920 to 1000 kg/m^3 (22.3° API to 10° API)
- Extra-heavy: greater than 1000 kg/m3 (less than 10° API)

Heavy or extra heavy crude oil as defined by the density ranges given, but with viscosity larger than 10 000 mPa.s measured at earlier temperature in the reservoir and atmospheric pressure, on a gas-free basis, would commonly be classified as bitumen. As recorded by the EIA data 2004, One barrel of crude oil contains 42 gallons about 46% of each barrel of crude oil is refined into automobile gasoline. In the US and Canada a mean of 3 gallons of crude oil are consumed per person each day. The US imports about 50% of its required crude oil and about 50% of that amount comes from OPEC countries. This study is illustrated in Table 2.2.

Table 2.2: The Production of one barrel of Crude Oil

Product	**Refined Gallons/Barrel**
Gasoline	19.3
Distillate Fuel Oil (Inc. Home Heating Diesel Fuel)	9.83
Kerosene Type Jet Fuel	4.24
Residual Fuel Oil	2.10
Petroleum Coke	2.10
Liquified Refinery Gases	1.89
Still Gas	1.81
Asphalt and Road Oil	1.13
Petrochemical Feed Supplies	0.97
Lubricants	0.46
Kerosene	0.21
Waxes	0.04
Aviation fuel	0.04
Other Products	0.34
Processing Gain	2.47

2.4 Effect of Heavy crude Oil in Pipeline

Another promising pipeline technique is the transport of viscous crudes as concentrated oil-in-water (O/W) emulsions. In this method, with the aid of suitable surfactants, the oil phase becomes dispersed in the water phase and stable oil-in-water emulsions are formed. The formation of an emulsion causes a significant reduction in the emulsion viscosity; even O/W emulsion might reduce corrosion with a crude oil with high sulphur content; corrosion may also appear with use of an aqueous phase, even with the use of formation water, rich in salts. The produced emulsions have viscosities in the range of approximately 0.05–0.2 Pa s. Because of this reduction in viscosity, the transportation costs and transport-assisted problems are reduced. This method can be very effective in the transportation of crude oils with viscosities higher than 1 Pa s especially in cold regions. In addition, because water is the continuous phase, crude oil has no contact with the pipe wall, which reduces pipe corrosion for crudes with high sulphur contents and prevents the deposition of sediments in pipes, as is common for crudes with high asphaltene contents.

According to Zaki., et al 1997, formation of oil-in-water emulsions to reduce the viscosity of heavy asphaltic crude oils and bitumen has been under investigation to provide an alternative to the function of diluent or the application of heat for viscosity reduction in pipelines. The oil-in-water emulsions is dominant in pipeline systems represents a radical departure from conventional practice. As a result, a number of potential are worthy of interest, consist the possibility of freezing, emulsion breakdown or inversion and demulsification of the emulsion after its transportation. Sayed (2012) studied said emulsions are defined as the colloidal systems in which fine droplets of one liquid are dispersed in another liquid where the two liquids otherwise being mutually immiscible. Oil Crude Oil Emulsions –and water produce emulsion by stirring. After all, the emulsion starts to break down immediately after stirring is stopped.

Emulsion stability depends on presence of adsorbed structures on the interface between the two liquid phases. Emulsion act is largely controlled by the properties of the adsorbed layers that stabilize the oil-water surfaces. There are three main criteria that are necessary for formation of crude oil emulsion:

1. Two immiscible liquids must be brought in contact;
2. Surface active component must present as the emulsifying agent;
3. Sufficient mixing or agitating effect must be provided in order to disperse one liquid to another as droplets.

During emulsion formation, the deformation of droplet is opposed by the pressure gradient between the external (convex) and the internal (concave) side of an interface. The gradient of pressure or velocity gradient required for emulsion formation is mostly supplied by agitation. The large excess of energy appropriated to produce emulsion of small droplets can only be supplied by very intense agitation, which needs much energy (Sayed., 2012).

2.5 Enhance-Oil Recovery (EOR)

This succinct review concentrates on crude oil-water emulsions stability proxies in the context of enhanced-oil recovery (EOR). If emulsions can act as mobility control agents, as hypothesized in this article, physicochemical conditions arising from injection of EOR fluid slugs into reservoirs are of the upmost relevance, if these conditions favour emulsion formation and stabilization. The issue of emulsion formation is set aside and we concentrate on issues of stability and consequently on stability proxies. Emulsions naturally arise in oilfield operations and understanding of stabilizing mechanisms is important. Figure 2.1 is a cartoon of the evolution steps that emulsions typically follow toward phase separation:

(1) Creaming or sedimentation, depending on the density contrast between the continuous and dispersed phases; (2) flocculation; (3) coalescence; (4) phase separation. Emulsion can lose significant structural integrity, through coalescence, before any phase separation occurs.

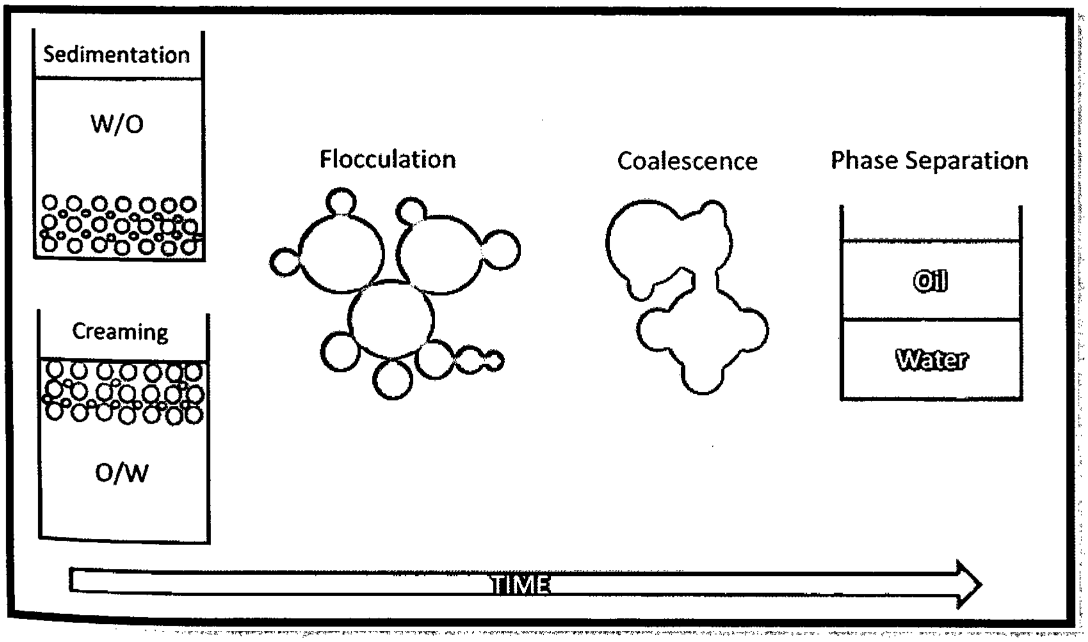

Figure 2.1: Step toward phase separation in oil in water separation.

Breaking oil-in-water emulsions associated with chemical processes such as surfactant-polymer and alkaline-surfactant-polymer flooding is relevant for the success of the EOR processes these emulsions can be very stable.

2.6 Emulsification

About 100 years ago, Bancroft proposed that when oil, water and surfactant are mixed, the continuous phase of the emulsion that forms is the phase where the surfactant is more soluble. When particles are used to stabilize emulsions, the Bancroft rule translates into a condition for the contact angle θ between the particle and the oil-water interface. If $\theta>90°$, the emulsion formed is W/O, if $\theta < 90°$, O/W; the contact angle should not be too far from 90°, otherwise the energy required to remove particles from the interface is small, and the emulsions are not very stable .For particles with $\theta \sim 90°$, both O/W and W/O emulsions can be made stable for long periods. Inversion occurs without hysteresis, by increasing or decreasing water volume fraction. This is in contrast to surfactant systems, where emulsions either do not invert (and form gel emulsions instead) or invert with a considerable hysteresis (as much as 0.3 in volume fraction). In addition, picker emulsions are most stable near inversion, unlike surfactant emulsions, which become notoriously unstable. The reason for these features is still unclear. There is a large variety of emulsification methods: simple shaking, mixing with rotor-stator systems, liquid injection through porous membranes, or high pressure devices (Walstra et al., 1993).

2.7 The Hydrophilic-Lipophilic Balance (HLB) Concept

Today, the selection of different surfactants in the preparation of either O/W or W/O emulsions is often made on an empirical basis. One such semi-empirical scale for selecting surfactants is the hydrophilic-lipophilic balance (HLB) number developed by Griffin. This scale is based on the relative percentage of hydrophilic to lipophilic (hydrophobic) groups in the surfactant molecule(s). For an O/W emulsion droplet the hydrophobic chain resides in the oil phase, while the hydrophilic head group resides in the aqueous phase. In contrast, for a W/O emulsion droplet the hydrophilic group(s) reside in the water droplet, whereas the lipophilic groups reside in the hydrocarbon phase. A guide to the selection of surfactants for particular applications is provided in Table 2.3. Here, the HLB number is seen to depend on the nature of the oil and, as an illustration, the required HLB numbers to emulsify various oils. The relative importance of the hydrophilic and lipophilic groups was first recognized when using mixtures of surfactants containing varying proportions of low and high HLB numbers. The efficiency of any combination (as judged by phase separation) was found to pass a maximum when the blend contained a particular proportion of the surfactant with the higher HLB number.

Table 2.3: Summary of surfactant HLB ranges and their applications

HLB range	**Application**
3-6	W/O emulsifier
7-9	Wetting agent
8-18	O/W emulsifier
13-15	Detergent
15-18	Solubilizer

2.8 Droplet size distribution

The droplet size distribution of the prepared emulsions using different speeds of mixing was determined by means of a computer controlled Coulter LS-100 Laser droplet size distribution analyzer. The emulsion samples containing formation water were diluted with formation water in order to obtain the appropriate obscuration value which should be in the range from 8% to 12%. The duration time for the run was shortened to 180 s because coalescence could occur during the measurements.

About 100 years ago, Bancroft proposed that when oil, water and surfactant are mixed, the continuous phase of the emulsion that forms is the phase where the surfactant is more soluble. When particles are used to stabilize emulsions, the Bancroft rule translates into a condition for the contact angle θ between the particle and the oil-water interface. If $\theta > 90°$, the emulsion formed is W/O, if $\theta < 90°$, O/W; the contact angle should not be too far from 90°, otherwise the energy required to remove particles from the interface is small, and the emulsions are not very stable. For particles with $\theta \sim 90°$, both O/W and W/O emulsions can be made stable for long periods. Inversion occurs without hysteresis, by increasing or decreasing water volume fraction. This is in contrast to surfactant systems, where emulsions either do not invert (and form gel emulsions instead) or invert with a considerable hysteresis (as much as 0.3 in volume fraction). In addition, picker emulsions are most stable near inversion, unlike surfactant emulsions, which become notoriously unstable. The reason for these features is still unclear.

2.9 Complex System

Many studies have been carried out in the last 40 years and have led to a deep understanding of those complex systems (Zaki et al., 2000). Despite there are still many unsolved questions connected to the peculiar behavior of these emulsions. The complexity comes mainly from the oil composition, in particular from the surface-active molecules contained in the crude. These molecules cover a large range of chemical structures, molecular weights, and HLB (Hydrophilic-Lipophilic Balance). Crude oils contain asphaltenes (high molecular weight polar components) that act as natural emulsifiers. Other crude oil components are also surface active: resins, fatty acids such as naphthenic acids, porphyrins, wax crystals, but most of the time they cannot alone produce stable emulsions. However, they can associate to asphaltenes and affect the stabilization of emulsion. Resins solubilize asphaltenes in oil and remove them from the interface, therefore lowering emulsion stability. However, they are probably partly responsible for the important dependence of emulsion stability upon water pH.

2.10 Oil–water phase inversion prediction

Phase inversion, in oil–water emulsion systems, refers to a phenomenon where, with a small change in the operational conditions, dispersion of oil drops in water (o/w) becomes dispersion of water drops in oil (w/o), or vice versa. This transition is usually associated with an abrupt change in the rates of momentum, heat and mass transfer between the continuous and dispersed phases and between the dispersion and the system solid boundaries. Since the rheological characteristics of the dispersion and the associated pressure drop change abruptly and significantly at or near the Phase Inversion Point (PIP), the PIP is a major factor to be considered in the design of oil–water transportation pipelines (Arirachakarn et al., 1989). Also, the corrosion of the pipe is determined to a large extent by the identity of the phase that wets it. The PIP is usually defined as the critical volume fraction (critical water fraction or critical oil fraction) of the dispersed phase above which this phase will become the continuous phase.

2.11 Demulsification

Demulsification is defined as a process of breaking emulsions with intention to separate water from oil (Fan, Simon & Sjoblom, et al., 2009). As been reported by Salager on 2006, the breaking of watering- petroleum emulsion still not totally understood even the researches have been done for decades ago. Thus, much study on this is still required. The mechanism of destabilization by using demulsifier is quite complicated. By that, there is no chemicals demulsifiers is applicable to break all kind of crude oil emulsion (Alwadani et al., 2009). There have three main methods to demulsify the emulsion namely mechanical, electrical and chemical. However, chemical method is most widely used (Wu, J & Xu, Y et al., 2003) .Basically, chemical demulsification is addition of small amount demulsifier (usually 1-1000ppm) intentioned to enhance phase separation (Fan, Simon & Sjoblom, et al., 2009).

2.12 Emulsion

An emulsion is formed when two immiscible liquid are mixed together. There are two basic type of emulsion namely water-in-oil (w/o) and oil-in-water (o/w). However, in some cases multiple emulsions such as water-in-oil-water (w/o/w) and oil-in-water-in-oil (o/w/o) emulsions can be found. There are three main criteria that play important role during emulsification process (Zulkania at el., 2004). First, in order to form an emulsion, it requires availability of two immiscible liquids. Secondly, emulsion is formed by applying mechanical energy to generate droplets. This is the critical step in emulsification process. The third criterion is the presence of an agent processing partial solubility in both phases which known as emulsifier. Therefore, the emulsifier will help to prevent water separation from a given w/o emulsion (Ghannam, M.T.at el., 2005).

2. 13 Breaking down process of Emulsion

This breakdown process was a summary of each of process occurs, together with details of each process and methods for its prevention. They are generally described as illustrated in Figure 2.2 below:

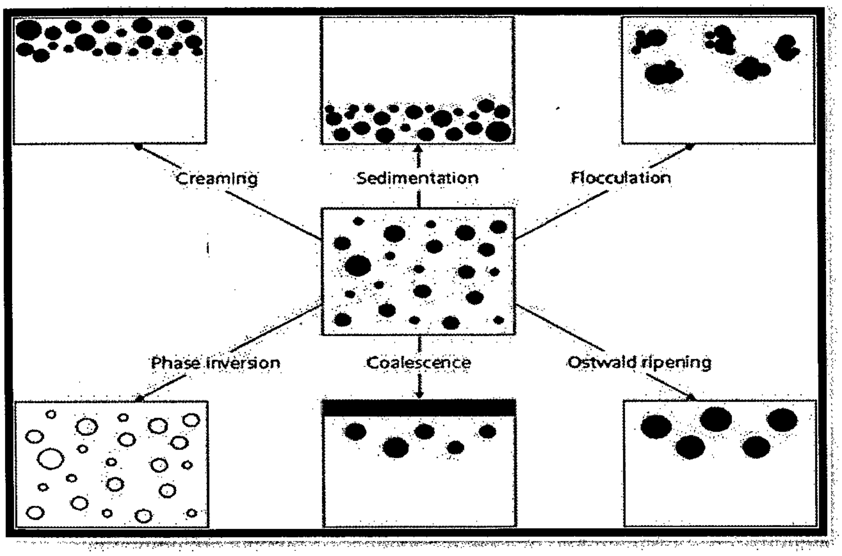

Figure 2.2: Breakdown Process of Emulsion

i. **Creaming and Sedimentation**: This process results from external forces, usually gravitational or centrifugal. When such forces exceed the thermal motion of the droplets (Brownian motion), a concentration gradient builds up in the system such that the larger droplets move more rapidly either to the top (if their density is less than that of the medium) or to the bottom (if their density is greater than that of the medium) of the container. In the limiting cases, the droplets may form a close-packed (random or ordered) array at the top or